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EXCIMER FORMATION OF A NAPHTHALENE DIISOCYANATE BASED

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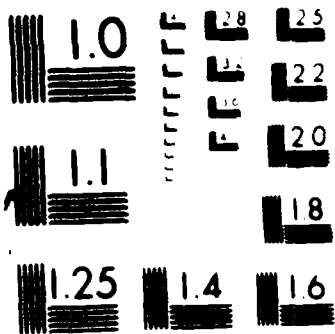
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Contract N00014-85-K-0748

Technical Report No. 11

AD-A183 728

EXCIMER FORMATION OF A NAPHTHALENE DIISOCYANATE BASED  
POLYURETHANE IN SOLUTION

by

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Prepared for Publication in  
Macromolecules

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AUG 05 1987  
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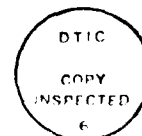
## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION NONE		1b. RESTRICTIVE MARKINGS NONE	
2a. SECURITY CLASSIFICATION AUTHORITY NONE		3. DISTRIBUTION/AVAILABILITY OF REPORT  UNLIMITED	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE NONE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S)  ONR #11		5. MONITORING ORGANIZATION REPORT NUMBER(S)  ONR N00014-85-K-0748	
6a. NAME OF PERFORMING ORGANIZATION University of Southern Mississippi	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION  Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) University of Southern Mississippi Polymer Science Department Southern Station Box 10076 Hattiesburg, MS 39406-0076		7b. ADDRESS (City, State, and ZIP Code)  800 North Quincy Avenue Arlington, VA 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code)  800 N. Quincy Avenue Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification)  Excimer Formation of a Naphthalene Diisocyanate Base Polyurethane in Solution.			
12. PERSONAL AUTHOR(S) C. E. Hoyle and K. J. Kim			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) 87/7/29	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION  Submitted, Macromolecules			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)  Naphthyl carbamates are shown to form excimers which are stabilized by hydrogen bonding inherent in the participating species. Substitution of a methyl group on the central nitrogen atom of the carbamate moiety severely limits excimer formation. A polyurethane based on 1,5-naphthalene diisocyanate forms intramolecular excimers in dilute solutions of both good and poor solvents; however, excimer formation is significantly enhanced in poor solvents where intramolecular contact between naphthyl carbamate groups is favored. The photophysics of excimer formation in the polyurethane is interpreted on the basis of an "isolated monomer" scheme. By measuring the excimer to monomer intensity ratio in pure and mixed solvent systems, the solubility parameter of the polymer is estimated to be between 21 and 22 $(\text{J/m}^3)^{1/2} \times 10^{-3}$ . $\leftarrow$			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL Charles E. Hoyle		22b. TELEPHONE (Include Area Code) (601)266-4868	22c. OFFICE SYMBOL

**EXCIMER FORMATION OF  
A NAPHTHALENE DIISOCYANATE BASED  
POLYURETHANE IN SOLUTION**

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## ABSTRACT

Naphthyl carbamates are shown to form excimers which are stabilized by hydrogen bonding inherent in the participating species. Substitution of a methyl group on the central nitrogen atom of the carbamate moiety severely limits excimer formation. A polyurethane based on 1,5-naphthalene diisocyanate forms intramolecular excimers in dilute solutions of both good and poor solvents; however, excimer formation is significantly enhanced in poor solvents where intramolecular contact between naphthyl carbamate groups is favored. The photophysics of excimer formation in the polyurethane is interpreted on the basis of an "isolated monomer" scheme. By measuring the excimer to monomer intensity ratio in pure and mixed solvent systems, the solubility parameter of the polymer is estimated to be between 21 and 22  $(\text{J/m}^3)^{1/2} \times 10^{-3}$ .

## INTRODUCTION

Excimers are defined as excited state complexes between two equivalent species, one of which is in the excited state prior to formation of the complex. Excimers have lower excited state energies than the monomeric chromophores of which they are comprised, and consequently are characterized by a red-shifted emission. Their lifetimes may be longer or shorter than the monomer species from whence they are derived.

Since their discovery in polymeric systems, excimers have continued to be a topic of significant activity. Several excellent reviews of excimer formation in polymer solutions and films have been published in recent years (1-3). In most of the reports of excimer formation in polymer systems to date, the excimers are comprised of fluorescent species attached as pendant chromophores to the polymer backbone. These polymers are capable of forming excimers between nearest and non-nearest neighbors. In contrast to the large number of reports of excimers formed from pendant fluorescent groups, there are only a few reports of excimers formed between interactive chromophores which are located at large distances from each other in the same polymer backbone (4-11).

We recently reported that polyurethanes based on 1,5-naphthalene diisocyanate form intramolecular excimers between two naphthyl carbamate groups located in the same polymer chain (10,11). By comparison of the fluorescence decay parameters with model naphthyl carbamates, it was suggested that an "isolated monomer" scheme could account for the complex photophysics of

these naphthyl containing polyurethanes. The extent of excimer formation was found to be related to the intrinsic viscosity of the dilute polymer solutions (10). In this paper, our earlier work is expanded and complete details of the effect of solvent on the photophysics of a 1,5-naphthalene diisocyanate based polyurethane. In particular, the ratio of excimer to monomer emission is used to predict the polymer solubility parameter. Additionally, by utilizing model compound studies, it is found that the strong degree of excimer formation between naphthyl carbamate chromophores can be attributed, at least in part, to a hydrogen bonding effect between participating chromophores.

## EXPERIMENTAL

### Materials

Dichloromethane, 1,2-dichloroethane, N,N'-dimethylformamide, cyclohexane, and benzene were purchased from Burdick and Jackson and used without further purification. Xylene (Baker), toluene (Baker), ethylbenzene (Gold Label, Aldrich), 1-butanol (Aldrich), 1,2-propanediol (Aldrich), 1,4-butanediol (Aldrich), and 2,3-butanediol (Aldrich), were used as received. Propylbenzene (Aldrich) was distilled prior to use. Deionized water was used.

### Equipment

Steady state emission spectra were recorded on a Perkin-Elmer 650-10S Fluorescence Spectrophotometer. UV spectra were obtained on a Perkin-Elmer 320 UV Spectrophotometer. Fluorescence decay curves were obtained on a single-photon-counting apparatus from Photochemical Research Associates. All



samples were thoroughly purged with nitrogen prior to fluorescence measurements. The data were analyzed by a software package obtained from PRA based on the iterative convolution method.  $^{13}\text{C}$  NMR spectra were obtained on a JEOL FX90Q, and FT-IR spectra were recorded on a Nicolet 5DX. The elemental analyses were conducted by M-H-W Laboratories of Phoenix, AZ.

Solutions containing the NDI-650 polyurethane in mixed solvents were prepared by dissolving the NDI-650 polyurethane in the good solvent component ( $\text{CH}_2\text{Cl}_2$  or DMF) followed by the addition of the non-solvent (cyclohexane or  $\text{H}_2\text{O}$ ). In order to ensure complete mixing of the two solvents, each solution was vigorously stirred before the fluorescence emission spectrum was obtained. In some instances, the initial fluorescence intensity ratio recorded immediately after the above mixing procedure changed upon solution aging. This phenomenon will be discussed in a separate paper dealing with fluorescence in mixed solvent systems.

#### Synthesis of Model Compounds

1,5 Naphthalene diisocyanate (NDI). To a stirring solution of p-dioxane (50 mL) containing 1,5-diaminonaphthalene (Fluka, 5.1 g) trichloromethyl chloroformate was added (Fluka, 17 g) in p-dioxane (15 mL) through an addition funnel under a nitrogen stream. A white precipitate was immediately observed. After addition, the temperature was increased to reflux. The HCl subsequently formed was removed by passing through water. After

1 hour, the solution turned clear and was allowed to react for another 3 hours. The p-dioxane was evaporated under reduced pressure and the resulting solid was vacuum sublimed twice to give the colorless crystals in 71% yield: mp 126-128° (lit<sup>12</sup>. mp 129.5-131°C); IR 3022, 2300, 1600, 1500  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  NMR 130.9, 128.7, 127.7, 124.2, 122.2 ppm (benzene); Anal.  $\text{C}_{12}\text{H}_6\text{N}_2\text{O}_2$  Calc. C, 68.57; H, 2.88; N, 13.33; Found C, 68.62; H, 2.91; N, 13.32.

Propyl 1-(N-Naphthyl)carbamate (PNC). Into 50 mL of an ethyl acetate (distilled and dried) solution of 1-naphthyl isocyanate (Aldrich, distilled, 10 g) was added 1-propanol (Baker, distilled and dried, 7.1 g) through an addition funnel. The temperature was increased to the reflux temperature of ethyl acetate and the mixture was allowed to react for 8 hours under a nitrogen stream. The precipitates were removed by filtration and ethyl acetate was evaporated under reduced pressure. The forming product was purified by recrystallization from  $\text{CH}_3\text{CN}$ : mp 72°C; IR 3325, 2950, 1675, 1600, 1540, 1500  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  NMR 156.1, 135.3, 129.1, 126.8, 126.6, 125.5, 123.4, 120.9, 67.1, 23.2, 10.9 ppm (DMF); Anal.  $\text{C}_{14}\text{H}_{15}\text{NO}_2$  Calc. C, 75.24; H, 6.59; N, 6.11; Found C, 75.36; H, 6.51; N, 6.18.

Propyl N-methyl N-(1-naphthyl) carbamate (PNMNC). For the preparation of this compound, all reactions were carried out in an ice bath. NaH (Alfa, 50% in oil, 1.2 g) was dispersed in DMF (Burdick & Jackson, dried, 5 mL) and the solution was cooled in an ice bath. The propyl N-(1-naphthyl) carbamate (3.3 g) in DMF

(15 mL) was added to a reactor through an addition funnel dropwise under a nitrogen stream. Immediately, hydrogen was generated and the reaction mixture turned green. The stirring was continued for 1.5 hours.  $\text{CH}_3\text{I}$  (Aldrich, distilled, 4.0 g) in DMF (10 mL) was added dropwise and the reaction mixture turned colorless. The solution was allowed to react for 2 hours. When the reaction was complete, the precipitates were removed by filtration and DMF was evaporated under reduced pressure. The residue was redissolved in diethylether, and the insolubles were removed by filtration. After evaporation of solvent, the resulting liquid was vacuum distilled. A colorless liquid was obtained; bp 120-125°C at 0.5 mm Hg; IR 3060, 2950, 1700, 1600, 1500  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  NMR 158.6, 142.9, 137.4, 133.3, 131.2, 130.4, 129.3, 128.9, 128.5, 127.7, 125.5, 69.5, 40.7, 25.0, 12.7 ppm (neat); Anal.  $\text{C}_{15}\text{H}_{19}\text{NO}_2$  Calc. C, 74.05; H, 7.04; N, 5.75; Found C, 74.16; H, 6.95; N, 5.69.

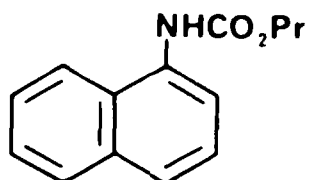
Dipropyl N,N'-naphthalene-1,5-diylbiscarbamate (1,5-DNB). To a p-dioxane solution containing 1-propanol (1.71 g) and dibutyltin dilaurate (Polysciences, 0.2 g) was added 1,5-naphthalene diisocyanate (1.5 g) at once. The reaction mixture was heated to 80°C and allowed to react for 4 hours with stirring under a nitrogen stream. After evaporation of p-dioxane, the forming product was purified by recrystallization from  $\text{CH}_3\text{CN}/\text{DMF}$  (50/50); mp 203°C; IR 3290, 3000, 1685, 1540, 1500  $\text{cm}^{-1}$ ; Anal.  $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2$  Calc. C, 65.44; H, 6.71; N, 8.48; Found C, 65.38; H, 6.63; N, 8.59.

Synthesis of NDI-Polyurethane (NDI-650). To 20 mL of 1,1,2,2-tetrachloroethane (Baker, distilled and dried) containing polytetramethylene ether glycol (Polysciences, average MW 650, 2.17 g), dibutyltin dilaurate (Polysciences, 0.11 g), and DABCO, (Aldrich, 0.08 g) was added 1,5-naphthalene diisocyanate (0.7 g). The mixture was heated to 100°C and allowed to polymerize for 2.5 hours with stirring under a nitrogen stream. The 1,1,2,2-tetrachloroethane was evaporated under reduced pressure and the products were dissolved in  $\text{CH}_2\text{Cl}_2$ . The  $\text{CH}_2\text{Cl}_2$  solution was poured dropwise into 500 mL of cyclohexane. The precipitated polymer was collected and dried; IR 3310, 2930, 1740, 1695, 1540, 1500  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  NMR 157.2, 136.2, 130.4, 128.4, 122.3, 120.3, 73.1, 67.9, 29.1, 28.6 ppm ( $\text{CH}_2\text{Cl}_2$ ); Anal. Calc. C, 65.71; H, 9.15; N, 3.26; Found C, 65.99 H, 9.32; N, 3.29. The molecular weight of NDI-650 was 51,000 by GPC.

## RESULTS AND DISCUSSION

Excimer Fluorescence of Model Naphthyl Carbamates. It is a well known phenomenon that concentrated naphthalene solutions exhibit emission from both monomer and excimer states (13, 14). Figure 1 shows the fluorescence spectra of naphthalene at several concentration in 1,2-dichloroethane. As the naphthalene concentration increases (curves b and c), a new broad fluorescence emission band appears with an emission maximum about 400 nm. (The spectra in Figure 1 are normalized to the monomer emission with maxima between 330 and 350 nm). This new red-shifted emission is attributed to excimer formation and its

intensity is dependent on the concentration of naphthalene. Results for the photophysics of concentrated naphthalene solutions have been thoroughly analyzed by a number of groups (13, 14) and will not be covered in this paper. If a propyl carbamate group is substituted on naphthalene in the 1 position, the monomer fluorescence (Figure 2) of the asymmetrical 1-(propyl N-naphthyl carbamate) (PNC) is characterized in dilute 1,2-dichloroethane solution (Figure 2, curve a) by a modest red-shifted (in comparison to naphthalene, Figure 1, curve a) monomer emission.

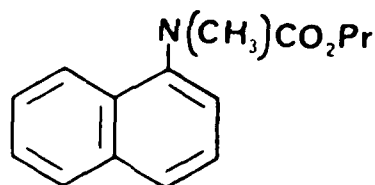


PNC

The decay curve of a dilute solution ( $1.31 \times 10^{-4} \text{ M}$ ) of PNC is single exponential with a lifetime ( $\tau_1$ ) of 3.8 ns (Table I). As in the case of naphthalene, when the concentration of PNC is increased the emission spectrum is red-shifted (Figure 2, curve b) as excimers are formed. Decay curves for both a dilute and a concentrated solution of PNC at wavelengths of monomer (330 nm) and excimer (480 nm) emission were recorded. For the concentrated solution (0.84 M), the decay curve obtained at 330 nm was readily fit to a double exponential decay function with parameters of 0.49 ns ( $\tau_2$ ) and 16.1 ns ( $\tau_3$ ). The lifetimes for

PNC in 1,2-dichloroethane are similar to those reported previously in dichloromethane and can be attributed to quenched monomer (0.49 ns) and excimer (16.1 ns) states (10). In addition to these results, by fitting the long lived portion of the excimer emission decay curve obtained at 480 nm, a decay parameter of 18.1 ns ( $\tau_3$ ) was obtained. From these studies, which are summarized in Table I, it can be concluded that PNC forms excimers in concentrated 1,2-dichloroethane solutions.

In contrast to the results for naphthalene and PNC in Figures 1 and 2, the emission spectrum of propyl N-methyl N-(1-naphthyl) carbamate (PNMNC -- see below) shows little red-shifted excimer emission, even at very high concentrations (Figure 3).



PNMNC

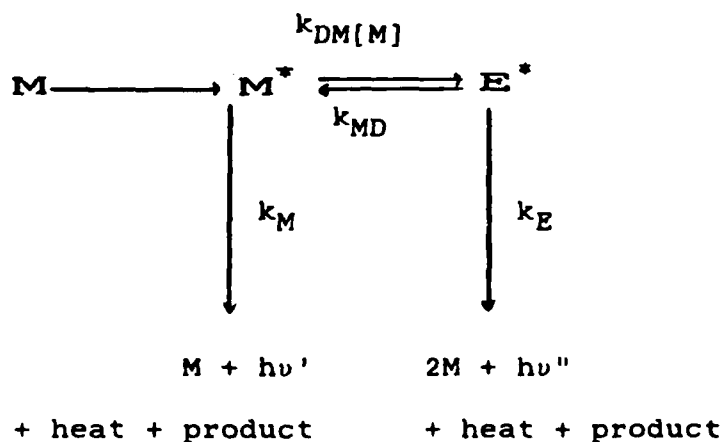
Apparently, the methyl group on the nitrogen of the carbamate chromophore hinders excimer formation. [Similar results for PNMNC in dichloromethane were recently reported (10)].

In order to contrast the results for PNC and PNMNC directly, plots of the excimer to monomer intensity ratio [ $I_{ex}/I_m$ ] versus concentration are given in Figure 4 for PNC, PNMNC, and naphthalene. From the results for PNC and PNMNC, it is quite obvious that methyl substitution greatly inhibits excimer

formation. The high degree of excimer formation for PNC versus naphthalene is particularly surprising when considered in light of the short monomer lifetime (3.8 ns) of PNC in 1,2-dichloroethane.

Before attempting to rationalize the high degree of excimer formation for PNC, one other piece of information must be considered; the rate of excimer formation. It has been established previously (10) that the PNC excimer in dichloromethane solution is formed according to the standard Birk's Scheme for excimer formation (Scheme I): where,

Scheme I



$k_M$  = non-radiative plus radiative rate constant for excited PNC monomer  $M^*$ .

$k_{DM}$  = rate constant for excimer formation between  $M$  and  $M^*$ .

$k_{MD}$  = rate constant for dissociation of excimer  $E^*$  into component species  $M^*$  and  $M$ .

$k_E$  = non-radiative plus radiative rate constant for excimer  $E^*$ .

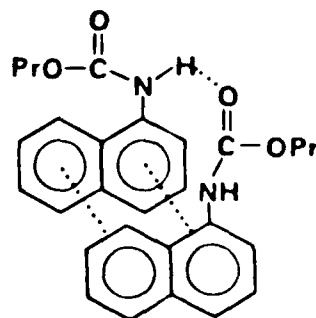
$M$  = ground state PNC.

$M^*$  = excited state PNC.

$E^*$  = PNC excimer.

The reciprocal of the decay constants for PNC monomer ( $\lambda_2 = 1/\tau_2$ ) and excimer ( $\lambda_3 = 1/\tau_3$ ) emission as a function of monomer concentration  $[M]$  have been calculated. Birks has shown that a plot of  $\lambda_2 + \lambda_3$  versus  $[M]$  should yield a straight line with slope equal to  $k_{DM}$ . The value of  $k_{DM}$  thus deduced from such a plot in Figure 5 is substantial ( $2.0 \times 10^9 \text{ s}^{-1}\text{M}^{-1}$ ).

In analyzing the results from Figures 4 and 5 one is forced to conclude that excimer formation for PNC is quite efficient. In comparing the results for PNC and PNMNC in Figure 4, a first analysis might attribute the low degree of excimer formation in PNMNC to steric hinderance afforded by methyl substitution. However, the carbamate group is already quite bulky before methyl substitution. One explanation for the efficiency of PNC excimer formation can be deduced by consideration of the well known hydrogen bonding phenomena (15) exhibited by aliphatic and aromatic urethanes. This is illustrated for PNC at high concentrations by the structure shown below



where the hydrogen connected to the central nitrogen of the urethane moiety of a PNC molecule forms a hydrogen bond to the carbonyl of the urethane group of a second PNC molecule. Such a



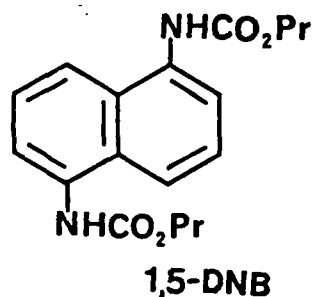
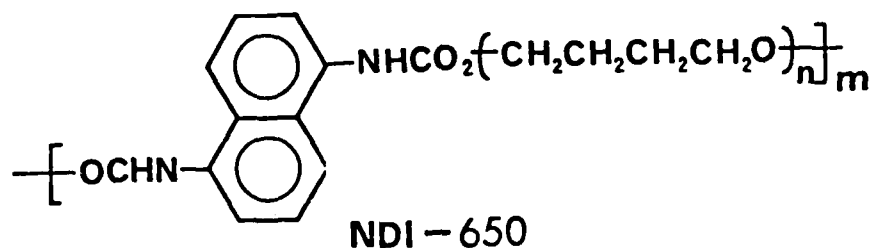
pre-existing structure prior to excitation of one the PNC molecules could account for the efficiency of excimer formation.

Evidence for hydrogen bonding in PNC solutions can be obtained by FT-IR analysis of the N-H stretching region. The unbonded N-H stretching in typical aryl urethanes has a strong IR band at  $\sim 3,400\text{ cm}^{-1}$  while hydrogen bonded N-H stretching has a somewhat red-shifted band ( $\sim 3,300\text{ cm}^{-1}$ ) resulting from a decrease in the resonant stretching frequency. Figure 6 shows a series of FT-IR spectra of PNC in 1,2-dichloroethane ranging from 0.5 M to 2.3 M. Both a non-bonded N-H ( $3,410\text{ cm}^{-1}$ ) and a hydrogen-bonded N-H ( $3,320\text{ cm}^{-1}$ ) absorbance are present in each spectra. The relative intensity of the hydrogen-bonded peak ( $I_{\text{bond}}$ ) increases linearly (Figure 7) with respect to the intensity of the free or non-bonded N-H ( $I_{\text{free}}$ ) as the PNC concentration increases. The increase in the  $I_{\text{bond}}/I_{\text{free}}$  ratio (Figure 7) over the same concentration as the  $I_{\text{ex}}/I_{\text{m}}$  ratio (Figure 4) increase leads to the postulation that excimer formation is enhanced by hydrogen bonding.

#### Excimer Fluorescence of Naphthalene Diisocyanate Based

Polyurethanes. Having shown that small molecule naphthyl carbamates form excimers quite efficiently, we turn to the more complex situation where naphthyl biscarbamate groups are spaced at regular repeating intervals on the backbone of a polymer chain. Figure 8 (curve b) shows the fluorescence spectrum of a very dilute 1,2-dichloroethane solution (0.01 g/dL) of a polyurethane (designated NDI-650) made from 1,5-naphthalene

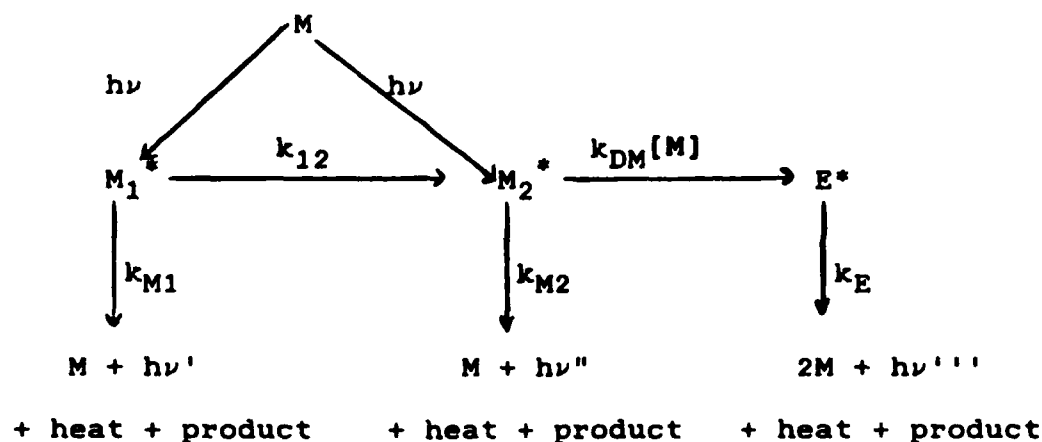
diisocyanate and polytetramethylene ether glycol (average MW 650). Comparison of the fluorescence from NDI-650 to that of a biscarbamate model compound dipropyl N,N'-naphthalene-1,5-diylbiscarbamate (1,5-DNB) in Figure 8 (curve a) ( $9.1 \times 10^{-5}$  M) reveals a red-shifted tail for NDI-650.



The absorption spectrum of 1,5-DNB (Figure 9, curve a) and NDI-650 (Figure 10, curve a) recorded on a conventional UV spectrometer reveals that the basic absorbing groups for both compounds are identical. Furthermore, the excitation spectra ( $\lambda_{em} = 430$  nm) recorded for PNB and NDI-650 (curve b in Figures 9 and 10) indicate that the emitting species is derived from the same basic type of absorbing chromophore. (Note that the small difference in the absorption and excitation spectra in Figures 9 and 10 can be attributed to the fact that the absorption spectra were recorded on a corrected dual beam UV spectrometer while the excitation spectrum were recorded on a single beam fluorescence

spectrometer uncorrected for wavelength response.) These results suggest that no specific interaction between ground state carbamate groups in the NDI-650 polyurethane exists before excitation. Additionally, the excimer is probably formed intramolecularly at the low concentrations employed (0.01 g/dL) (see Reference 10 for discussion).

The fluorescence decay curve for a dilute solution of PNB in 1,2-dichloroethane can be fit to a single exponential decay curve with a lifetime of 1.81 ns (Table II). We recently reported a similar value of 1.84 ns for 1,5-DNB in dichloromethane (10,11). In contrast to the concentrated PNC solution, the decay curve for a dilute solution (0.01 g/dL) of NDI-650 monitored at 330 nm in the monomer emission region cannot be fit to a double exponential decay function. Rather, the NDI-650 decay curve (330 nm) is fit by a triple exponential decay function with decay constants of 1.18 ns, 2.04 ns, and 15.5 ns. A value for the long-lived component of 17.9 ns was calculated by fitting a single exponential function to the long-lived portion of the decay curve obtained at 480 nm in the excimer region. Identical behavior has been reported in a recent paper (10) for NDI-650 in dichloromethane and can be interpreted by the "isolated monomer" scheme first reported by Phillips et. al. (16) and Holden et. al (17) to account for the excimer kinetics in naphthalene containing polymers. This photophysical mechanism is reproduced in Scheme II below:

Scheme II

where,

$k_{M1}$  = non-radiative plus radiative rate constant for excited isolated naphthyl monomer  $M_1^*$ .

$k_{M2}$  = non-radiative plus radiative rate constant for excited excimer forming naphthyl monomer  $M_2^*$ .

$k_{DM}$  = rate constant for excimer formation between  $M_2^*$  and  $M$ .

$k_{MD}$  = rate constant for dissociation of excimer  $E$  into component species  $M_2^*$  and  $M$ .

$k_E$  = non-radiative plus radiative rate constant for excimer  $E^*$ .

$k_{12}$  = rate constant for formation of excited excimer forming naphthyl monomer  $M_2^*$  from the excited isolated naphthyl monomer  $M_1^*$ .

$M$  = ground state naphthyl monomer.

$M_1^*$  = excited isolated naphthyl monomer.

$M_2^*$  = excited excimer forming naphthyl monomer.

Since this scheme is well documented, only a brief synopsis will be given here. Basically a ground state monomer ( $M$ ) upon excitation either forms: (1) an excited non-interactive monomer  $M_1^*$  which decays to the ground state by a radiative/non-radiative decay process, or (2) an interactive excited monomer  $M_2^*$  which

combines with a ground state monomer to give the excimer  $E^*$ . In the present case for NDI-650, the isolated monomer lifetime ( $\tau_1$ ) is 2.04 ns, in close agreement with the monomer lifetime of 1.81 ns for the 1,5-DNB model compound. The lifetime ( $\tau_2$ ) of the interactive monomer is 1.18 ns reflecting quenching of the monomer lifetime by a factor of about 33%. In order to provide additional evidence for the mechanism in Scheme II, fluorescence decay curves were recorded and analyzed for PNB and NDI-650 in several pure solvent systems. The results shown in Table III illustrate the strong agreement between the isolated monomer lifetime ( $\tau_1$ ) and the lifetime of the model compound 1,5-DNB ( $\tau_{\text{DNB}}$ ) in each solvent system employed. Such a correlation between  $\tau_1$  and  $\tau_{\text{DNB}}$  in eight solvents lends support to the "isolated monomer" scheme for the NDI-650 polymer in dilute solution.

Since the excimer fluorescence of NDI-650 in dilute solution can be attributed to an intramolecular process, it should be responsive to solvent induced changes in the conformational geometry of the polymer backbone. A preliminary paper (10) confirms this postulation for NDI-650 in dichloromethane, benzene, and xylene where it was reported that the excimer ( $I_{\text{ex}}$ ) to monomer ( $I_{\text{m}}$ ) intensity ratio increases in the order  $I_{\text{ex}}/I_{\text{m}}$  (dichloromethane) <  $I_{\text{ex}}/I_{\text{m}}$  (benzene) <  $I_{\text{ex}}/I_{\text{m}}$  (xylene) paralleling the decrease in the solvent solubility parameter and the intrinsic viscosity of the solution. In order to extend these results, the ratio  $I_{\text{ex}}/I_{\text{m}}$  was recorded for each of these three solvents (Figure 11) as a function of the NDI-650 polymer

at a critical concentration ( $C_{crit}$ ) which is directly dependent on the solvent system used. The value for  $C_{crit}$  increases with an increase in the solvent solubility parameter and solution intrinsic viscosity. Thus, in dichloromethane, which is a "good" solvent for NDI-650, a much higher polymer concentration (1.0 g/dL) must be employed before the occurrence of intermolecular interaction between naphthyl carbamate groups on different polymer chains. Conversely, in xylene and benzene (relatively poor solvents) intermolecular chain association takes place at much lower polymer concentrations. However, in both xylene and benzene the extent of intermolecular interaction, as indicated by the ultimate  $I_{ex}/I_m$  ratio, is quite low since precipitation occurs almost simultaneously with intermolecular contact. For NDI-650 in dichloromethane, even though high concentrations are required to reach the point for intermolecular association, the extent of intermolecular interaction is much larger as reflected by the  $I_{ex}/I_m$  ratio.

In order to extend the solvent studies, NDI-650 fluorescence spectra were recorded in a large number of pure solvents with varying solubility parameters. The resulting  $I_{ex}/I_m$  values are presented in Table IV. The highest  $I_{ex}/I_m$  value is in propyl benzene which has the lowest solubility parameter. The  $I_{ex}/I_m$  ratio reaches a minimum in 2,3-butanediol which has a solubility parameter of  $22.7 (J/M^3)^{1/2} \times 10^{-3}$ . A plot of  $I_{ex}/I_m$  versus solvent solubility parameter for the data in Table IV (as well as data from other solvents) is shown in Figure 12. A minimum value of  $\sim 21 \pm 2 (J/m^3)^{1/2} \times 10^{-3}$  can be construed as the polymer

solubility parameter.

Results similar to those obtained for the pure solvent systems can also be derived from fluorescence spectra of NDI-650 in mixed or co-solvent systems. For this study, two dual solvent systems were selected, each comprised of a good solvent and a non-solvent. The first dual solvent system consists of a good solvent (dichloromethane) and a non-polar non-solvent (cyclohexane). The second system consists of a good solvent (N,N-dimethylformamide) (DMF) and a polar non-solvent (water). Fluorescence spectra of NDI-650 in selected dichloromethane/cyclohexane and DMF/H<sub>2</sub>O solvents are shown in Figures 13 and 14. In each case as the percentage of non-solvent (cyclohexane in Figure 13 and H<sub>2</sub>O in Figure 14) is increased, the relative excimer fluorescence increases. (The spectra in Figures 13 and 14 are all normalized to maintain a constant intensity for the monomer emission). Tables V and VI list  $I_{ex}/I_m$  values and solubility parameters (estimated from the solubility parameters of the pure solvents) for a series of dichloromethane/cyclohexane and DMF/H<sub>2</sub>O co-solvent systems. A plot (Figure 15) of  $I_{ex}/I_m$  versus solvent solubility parameters for the combined data in Tables V and VI results in a minimum value for  $I_{ex}/I_m$  of approximately  $22 \pm 2 (J/m^3)^{1/2} \times 10^{-3}$ . This value agrees within experimental error with the minimum value obtained from Figure 12 for the pure solvent systems and confirms a polymer solubility parameter for NDI-650 of about  $21-22 (J/m^3)^{1/2} \times 10^{-3}$ .

## CONCLUSIONS

This paper deals with excimers formed between naphthyl carbamate groups spaced along the backbone of a polyurethane prepared from 1,5-naphthalene diisocyanate and polytetramethylene ether glycol (average MW = 650 g/mol). Model compounds have been extensively investigated to provide a basis for interpretation of the polymer systems. Specific findings reported in this paper are summarized below:

- (1) Propyl N-(1-naphthyl) carbamate (PNC) exhibits strong excimer emission at higher concentrations. By contrast propyl N-methyl N-(1-naphthyl) carbamate (PNMNC), which has a methyl group substituted on the central nitrogen atom of the carbamate group, has little excimer emission even at very high concentrations.
- (2) The degree of excimer formation of PNC correlates directly with the extent of hydrogen bonding in the system.
- (3) The NDI-650 polyurethane forms solvent dependent intramolecular excimers between carbamate groups on the same polymer at low concentrations.
- (4) The critical NDI-650 concentration required for intermolecular excimer formation is dependent on the "goodness" of the solvent medium, i.e., the critical concentration is 1 to 2 orders of magnitude larger for a good solvent such as dichloromethane.
- (5) The photophysical results support an "isolated monomer" scheme for intramolecular excimer formation in the NDI-650 polyurethane.
- (7) The variation of the excimer ( $I_{ex}$ ) to monomer ( $I_m$ ) intensity ratio with the solvent solubility parameter leads to an estimation of the polymer solubility parameter of  $21-22 (J/m^3)^{1/2} \times 10^{-3}$ .

This is one of the first detailed accounts of the photophysics of a polymer with the interacting excimer forming chromophores in the backbone. It suggests that a wealth of critical information concerning polymer structure can be obtained



by careful investigation of intramolecular excimer photophysics. Future work in this area will contrast the photophysics of polyurethanes and polyureas.

**ACKNOWLEDGMENT.** This work was sponsored by the Office of Naval Research.

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TABLE I. Fluorescence decay parameters of propyl 1-(N-naphthyl) carbamate in 1,2-dichloroethane<sup>a</sup>

<u>Concentration (M)</u>	<sup>b</sup> <u><math>\tau_1</math>(ns)</u>	<sup>c</sup> <u><math>\tau_2</math>(ns)</u>	<u><math>\tau_3</math>(ns)</u>
$1.31 \times 10^{-4}$	3.8	---	---
0.84	---	0.49	18.1 <sup>d</sup>

- a. N<sub>2</sub> atmosphere,  $\lambda_{ex} = 300$  nm; monitoring wavelength = 330 nm except where noted.
- b. Unquenched monomer lifetime.
- c. Quenched monomer lifetime.
- d. Excimer lifetime; monitoring wavelength is 480 nm.

TABLE II. Fluorescence decay parameters for PNB and NDI-650 in 1,2-dichloroethane<sup>a</sup>.

Compound	Concentration (g/dL)	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_3$ (ns)
1,5-DNB	0.01	1.81	--	--
NDI-650	0.01	2.04	1.18	15.5(17.9) <sup>b</sup>

a. Nitrogen atmosphere;  $\lambda_{\text{ex}}$  = 310 nm; monitoring wavelength is 330 nm except where noted.

b. Monitoring wavelength is 480 nm.

TABLE III. Fluorescence decay parameters of NDI-650 in various solvents<sup>a</sup>

Solvent	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_3$ (ns)	$\tau_{\text{DNB}}^f$	Solubility Parameter <sup>g</sup>
DMF <sup>b</sup>	2.38	1.41	13.4(12.8) <sup>e</sup>	2.36	24.8
DMF/H <sub>2</sub> O(70/30) <sup>c</sup>	2.60	0.44	18.1(23.9)	2.58	32.0
Toluene <sup>b</sup>	2.30	1.13	32.6(27.8)	2.20	18.3
DMF/H <sub>2</sub> O(80/20) <sup>c</sup>	2.56	0.62	16.1(21.6)	2.47	29.0
1-Butanol <sup>b</sup>	2.41	1.22	22.9(22.3)	2.48	23.3
1,2-propanediol <sup>d</sup>	2.67	0.84	18.8(18.1)	2.57	26.0
Benzene <sup>b</sup>	2.43	1.25	22.3(24.9)	2.30	18.8
Dichloromethane	2.04	1.20	19.2(21.4)	1.84	19.8

a.  $\lambda_{\text{ex}} = 310$  nm;  $\lambda_{\text{em}} = 330$  nm; nitrogen atmosphere.

b. 0.01 g/dL.

c.  $1.5 \times 10^{-3}$  g/dL.

d. Less than 0.01 g/dL; fluorescence emission spectrum was obtained from the solution which was filtered after heating at 60°C for 30 minutes.

e. The value in parenthesis signifies the lifetime of the longlived component when monitored at 480 nm.

f. Lifetime of 1,5-DNB.

g. Units of  $(\text{J/m}^3)^{1/2} \times 10^{-3}$ .

TABLE IV. Ratio of excimer to monomer intensity of NDI-650 in solvents with various solubility parameters.<sup>a</sup>

<u>Solvent</u>	$I_{ex}^e/I_m^f$	<u>Solubility Parameter<sup>g</sup></u>
Propyl benzene <sup>b</sup>	0.55	17.6
Xylene <sup>c</sup>	0.47	18.0
Benzene <sup>c</sup>	0.35	18.8
Dichloromethane <sup>c</sup>	0.21	19.8
2,3-Butanediol <sup>d</sup>	0.11	22.7
1-Butanol <sup>c</sup>	0.18	23.3
1,2-Propanediol <sup>d</sup>	0.27	25.8

a. Nitrogen atmosphere;  $\lambda_{ex} = 310$  nm.

b.  $5 \times 10^{-3}$  g/dL.

c. 0.01 g/dL.

d. Less than 0.01 g/dL; fluorescence emission was obtained from the solution which was filtered after heating at 60° C for 30 minutes.

e. Monitored at 430 nm.

f. Monitored at 355 nm.

g. Units of  $(J/m^3)^{1/2} \times 10^{-3}$ .

TABLE V. Ratio of excimer to monomer intensity of NDI-650 in the dichloromethane/cyclohexane mixed solvent system<sup>a</sup>.

(Dichloromethane/ Cyclohexane) <sup>b</sup>	$I_{ex}^c/I_m^d$	Solubility parameter <sup>e</sup>
1/1	0.23	18.3
7/13	0.34	17.9
6/14	0.41	17.7
5/15	0.45	17.6
4/16	0.60	17.4
3/17	0.69	17.3
2/18	0.98	17.1

a. Air atmosphere;  $5 \times 10^{-5}$  g/dL concentration;  $\lambda_{ex} = 300$  nm; fluorescence was measured in air atmosphere because bubbling with  $N_2$  affected the emission behavior of this mixed solvent system.

b. Volume ratio of dichloromethane to cyclohexane.

c. Monitored at 430 nm.

d. Monitored at 355 nm.

e. Units of  $(J/m^3)^{1/2} \times 10^{-3}$ ; calculated from solubility parameters of dichloromethane and cyclohexane.

TABLE VI. Ratio of excimer to monomer intensity of NDI-650 in the DMF/H<sub>2</sub>O mixed solvent system<sup>a</sup>

(DMF/H <sub>2</sub> O) <sup>b</sup>	$I_{\text{ex}}^{\text{c}}/I_{\text{m}}^{\text{d}}$	Solubility Parameter <sup>e</sup>
95/5	0.12	26.0
90/10	0.19	27.1
85/15	0.32	28.3
80/20	0.55	29.4
70/30	0.91	31.7
60/40	1.48	34.0

a. Nitrogen atmosphere;  $1.5 \times 10^{-3}$  g/dL concentration; this system is stable enough not to be affected by nitrogen bubbling.

b. Volume ratio of DMF to H<sub>2</sub>O.

c. Monitored at 430 nm.

d. Monitored at 355 nm.

e. Units of  $(\text{J/m}^3)^{1/2} \times 10^{-3}$ ; calculated from solubility parameters of DMF and water.



### Figure Captions

- Figure 1. Steady state fluorescence spectra ( $\lambda_{\text{ex}} = 300 \text{ nm}$ ) of naphthalene at various concentrations in 1,2-dichloroethane (curve a,  $3.9 \times 10^{-4} \text{ M}$ ; curve b,  $0.9 \text{ M}$ ; curve c,  $2.8 \text{ M}$ ).
- Figure 2. Steady state fluorescence spectra ( $\lambda_{\text{ex}} = 300 \text{ nm}$ ) of PNC in 1,2-dichloroethane (curve a,  $1.31 \times 10^{-4} \text{ M}$ ; curve b,  $1.9 \text{ M}$ ).
- Figure 3. Steady state fluorescence spectra ( $\lambda_{\text{ex}} = 280 \text{ nm}$ ) of PNMNC in 1,2-dichloroethane (curve a,  $4.1 \times 10^{-4} \text{ M}$ ; curve b,  $2.2 \text{ M}$ ; curve c,  $3.3 \text{ M}$ ).
- Figure 4. Ratios of excimer ( $I_{\text{ex}}$ ) to monomer ( $I_{\text{m}}$ ) intensity of model compounds as a function of concentration in 1,2-dichloroethane: ( $I_{\text{ex}} = 430 \text{ nm}$  (PNC),  $415 \text{ nm}$  (PNMNC),  $385 \text{ nm}$  (naphthalene);  $I_{\text{m}} = 355 \text{ nm}$  (PNC),  $340 \text{ nm}$  (PNMNC),  $325 \text{ nm}$  naphthalene.  $I_{\text{ex}}/I_{\text{m}}$  is corrected by a fluorescence spectrum of each compound in a dilute solution ( $9.5 \times 10^{-4} \text{ M}$  for PNC,  $7.8 \times 10^{-3} \text{ M}$  for PNMNC, and  $3.9 \times 10^{-4} \text{ M}$  for naphthalene).
- Figure 5. A plot of ( $\lambda_2 + \lambda_3$ ) of PNC as a function of concentration in 1,2-dichloroethane.
- Figure 6. IR spectra of PNC at various concentrations in 1,2-dichloroethane.
- Figure 7. A plot of  $I_{\text{bond}}/I_{\text{free}}$  as a function of PNC concentration in dichloroethane.
- Figure 8. Steady state fluorescence spectra ( $\lambda_{\text{ex}} = 300 \text{ nm}$ ) of 1,5-DNB (curve a,  $9.1 \times 10^{-5} \text{ M}$ ) and NDI-650 (curve b,  $0.01 \text{ g/dL}$ ) in 1,2-dichloroethane.
- Figure 9. Absorption spectrum (curve a,  $9.1 \times 10^{-5} \text{ M}$ ) and excitation spectrum (curve b,  $9.1 \times 10^{-5} \text{ M}$ ,  $\lambda_{\text{em}} = 430 \text{ nm}$ ) of 1,5-DNB in 1,2-dichloroethane.
- Figure 10. Absorption spectrum (curve a,  $0.01 \text{ g/dL}$ ) and excitation spectrum (curve b,  $1.7 \times 10^{-3} \text{ g/dL}$ ,  $\lambda_{\text{em}} = 430$ ) of NDI-650 in 1,2-dichloroethane.
- Figure 11. Ratio of excimer to monomer intensity as a function of NDI-650 concentration in various solvents.
- Figure 12. Ratio of excimer to monomer of NDI-650 as a function of solvent solubility parameter.  
(1. Propylbenzene; 2. Xylene; 3. Ethylbenzene; 4. Toluene; 5. Benzene; 6. Dichloromethane; 7. 1,2-Dichloroethane; 8.

2,3-Butanediol; 9. 1-Butanol; 10. 1,4-Butanediol; 11. 1,2-propanediol).

Figure 13. Steady state fluorescence spectra ( $\lambda_{ex} = 300$  nm) of NDI-650 in the mixed  $CH_2Cl_2$ /cyclohexane solvent systems ( $5 \times 10^{-5}$  g/dL). Curve a, 100% dichloromethane; curve b, cyclohexane/dichloromethane (70/30 vol. %); curve c, cyclohexane/dichloromethane (80/20 vol. %); curve d, cyclohexane/dichloromethane (90/10 vol. %).

Figure 14. Steady state fluorescence spectra ( $\lambda_{ex} = 300$  nm) of NDI-650 in DMF (curve a) and DMF/ $H_2O$  (70/30 vol. %) (curve b) solvent systems ( $1.5 \times 10^{-3}$  g/dL).

Figure 15. Ratio of excimer to monomer intensity in NDI-650 as a function of the solubility parameter of the mixed solvent systems.

Fig. 1

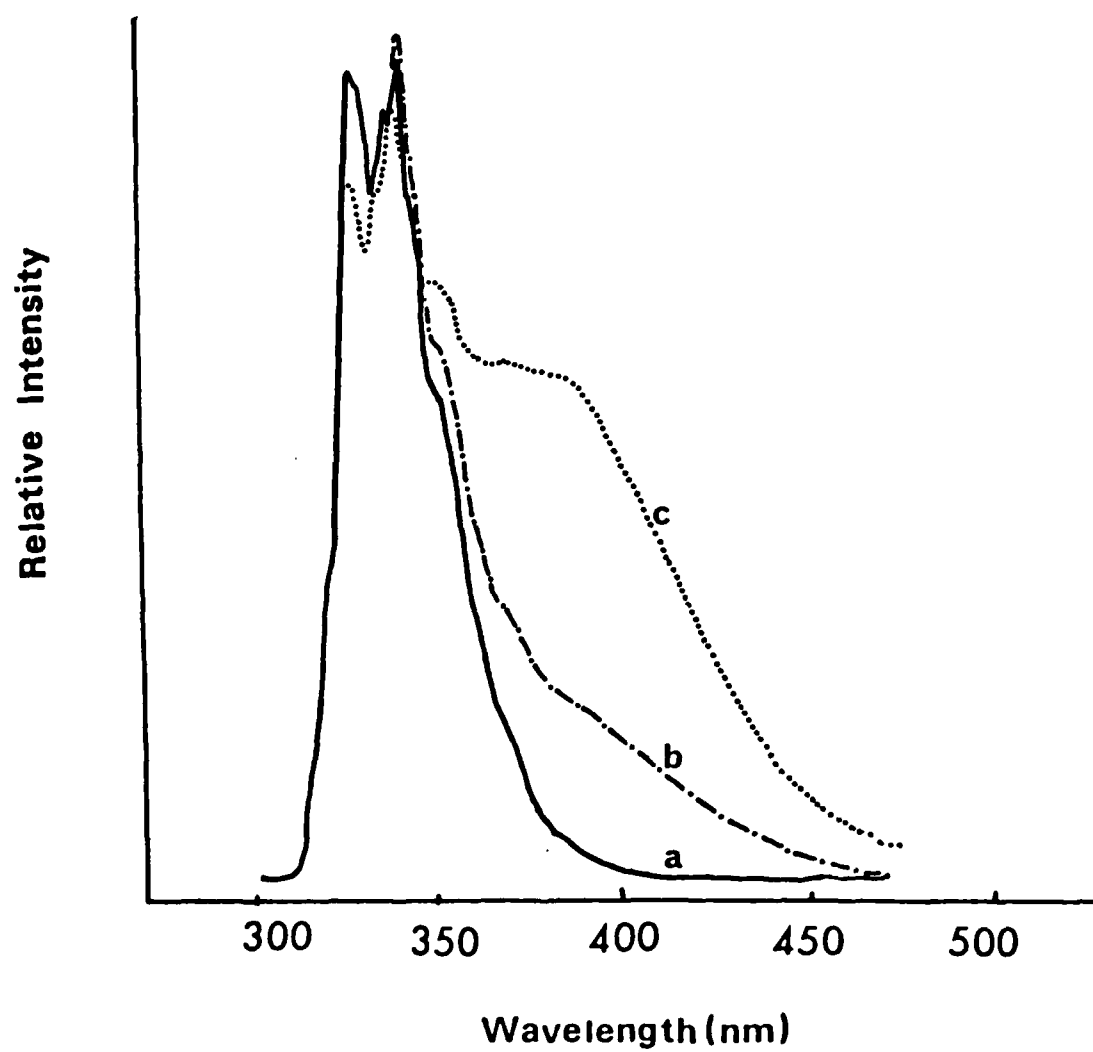


Fig. 2

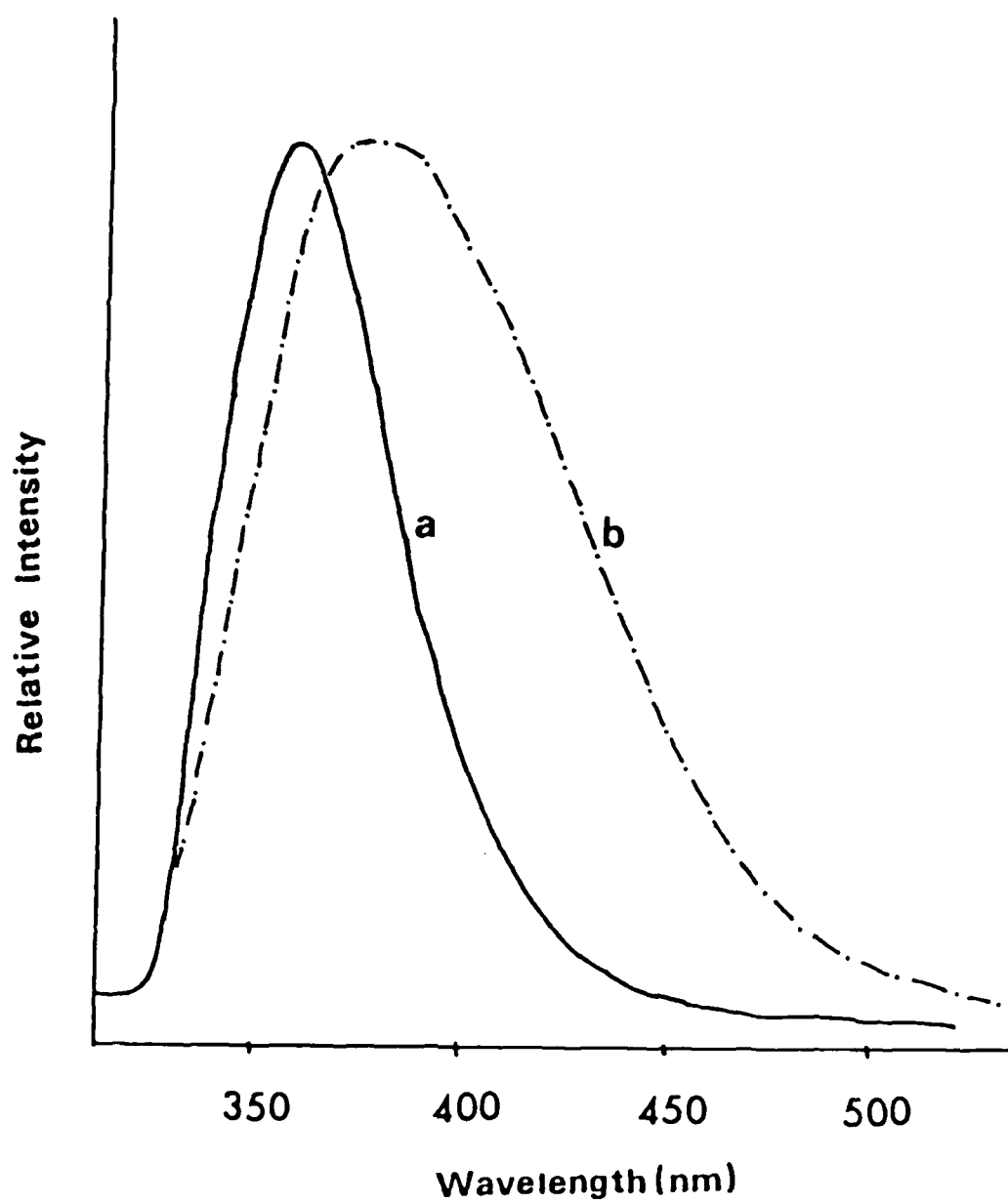


Fig. 3

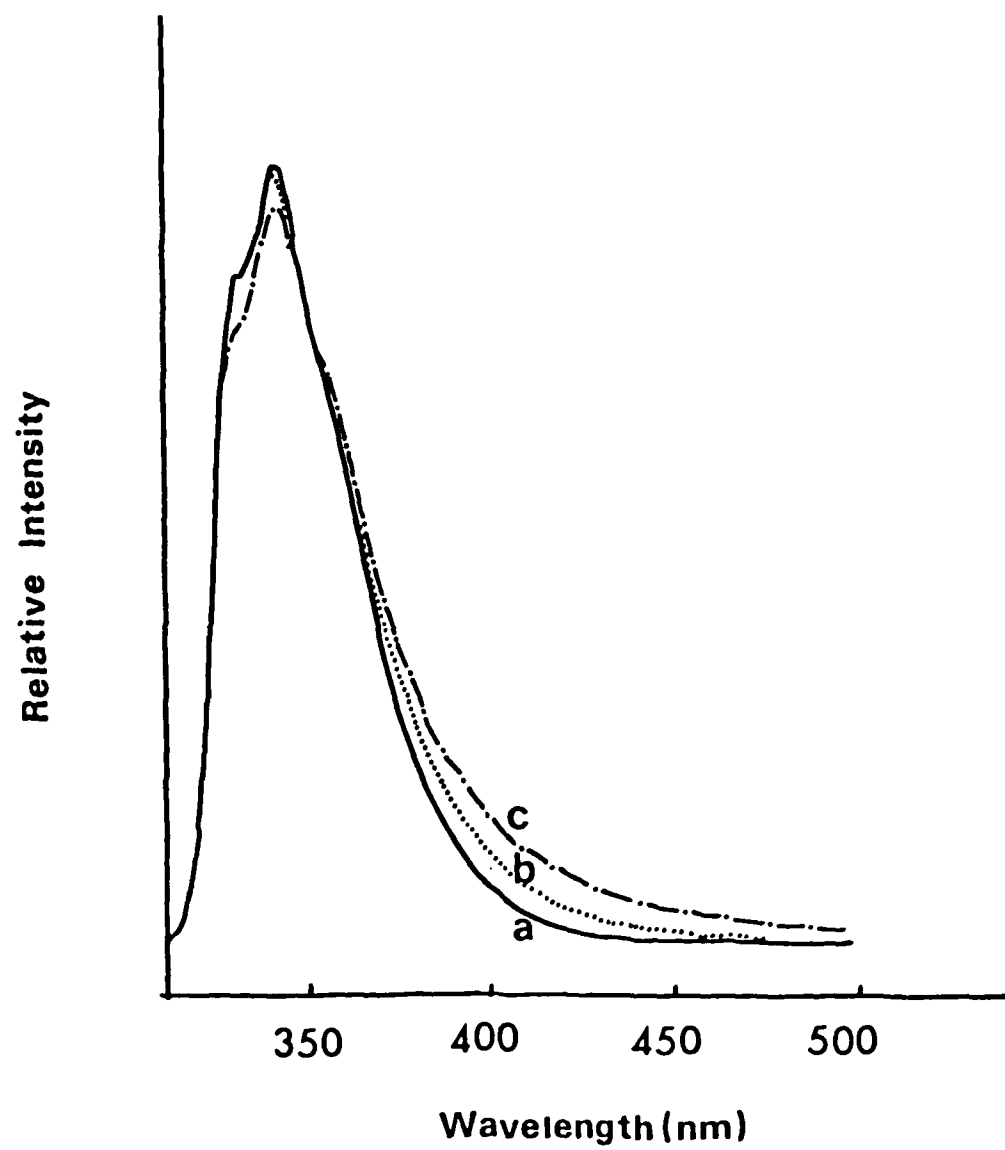


Fig. 4

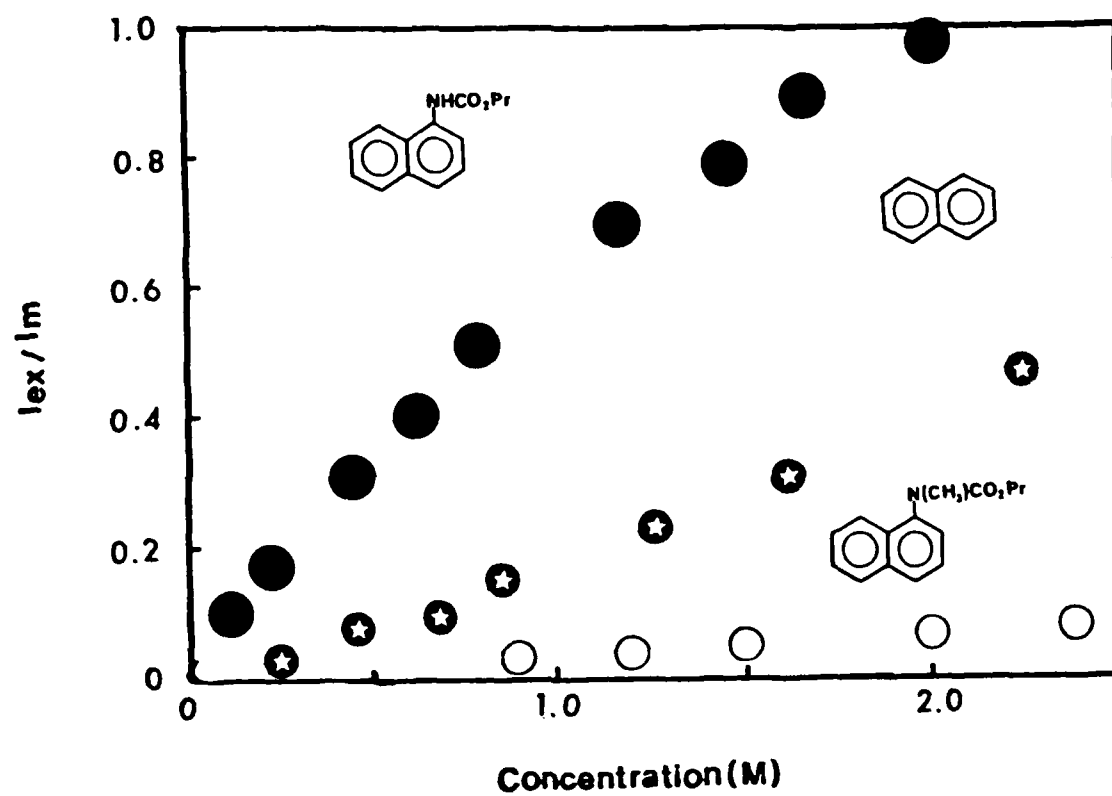


Fig. 5

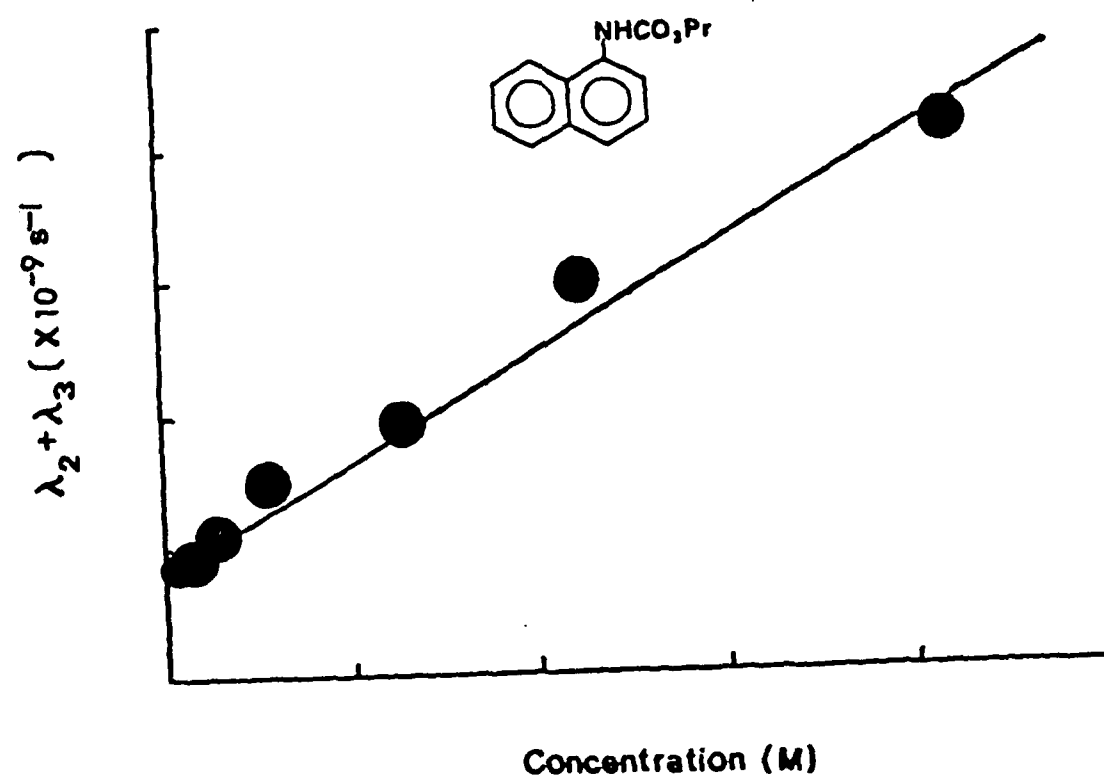


Fig. 1

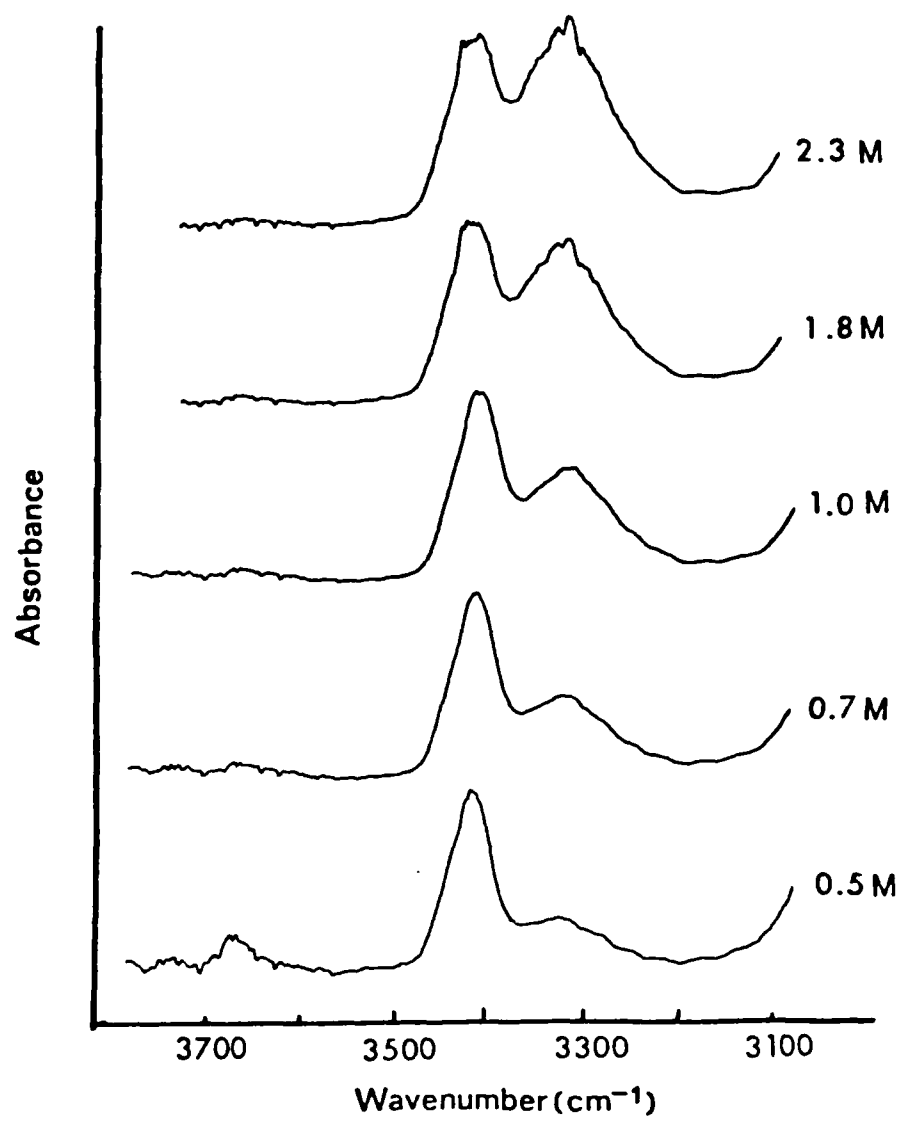




Fig. 7

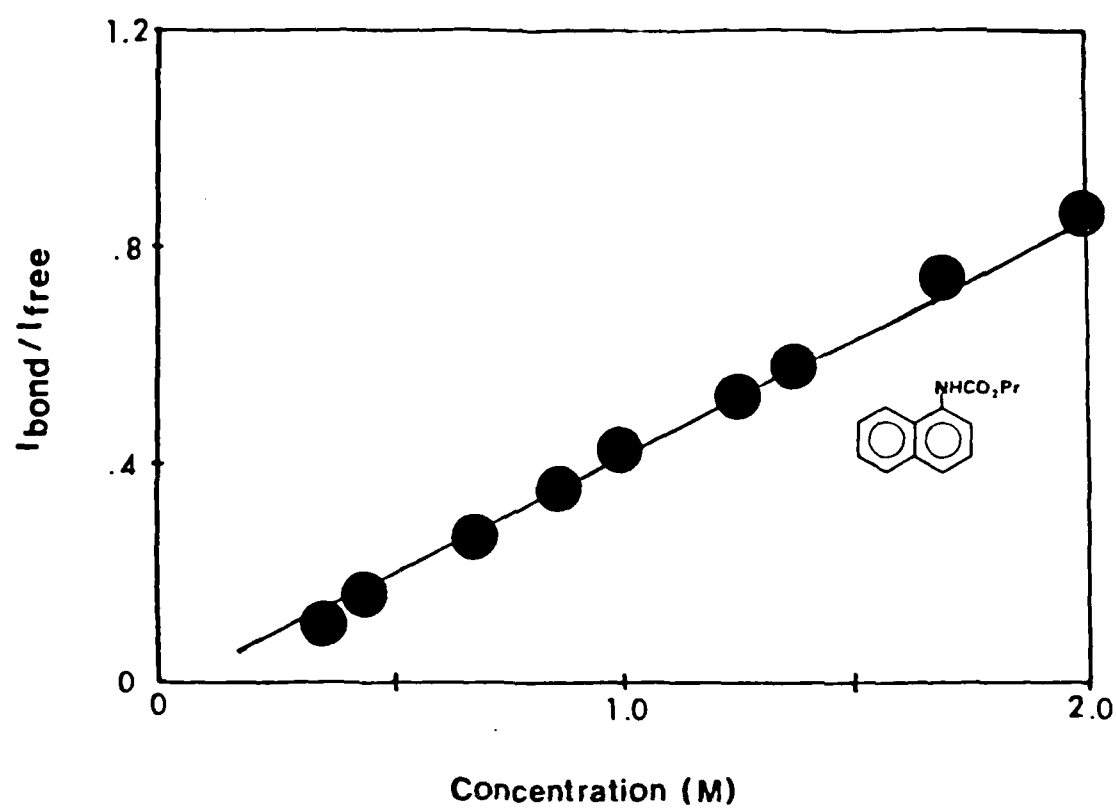


Fig. 8

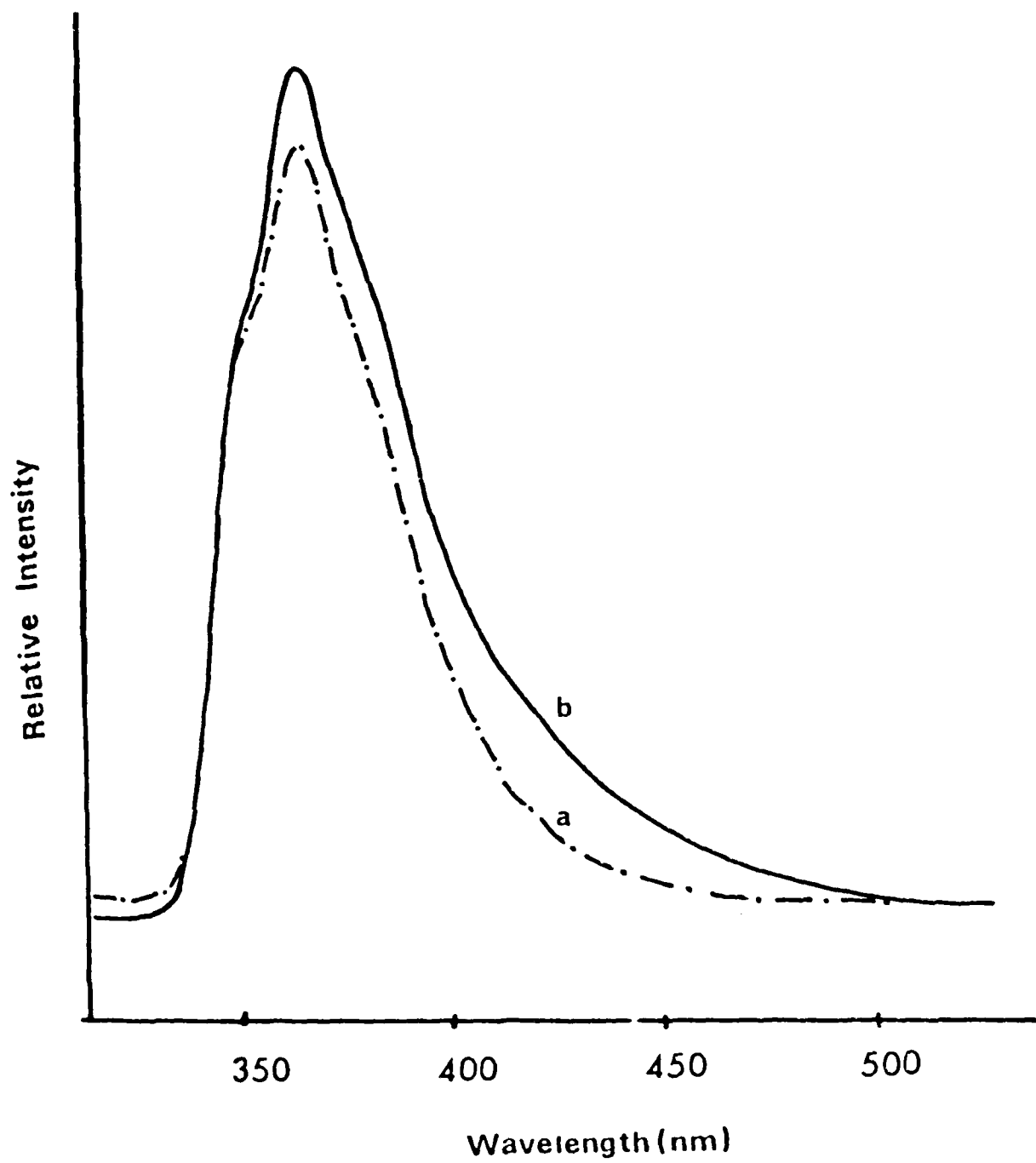


Fig 9

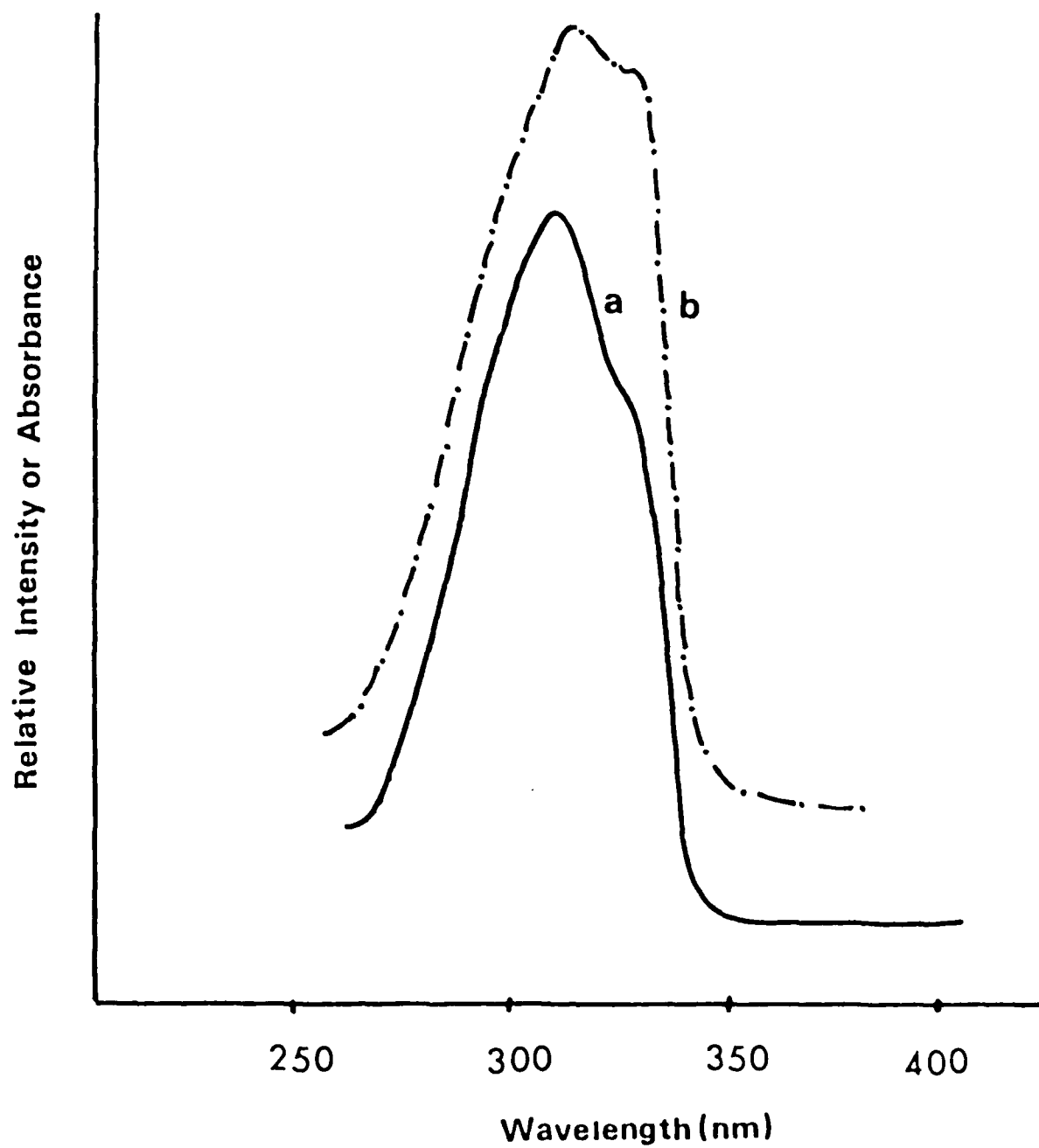
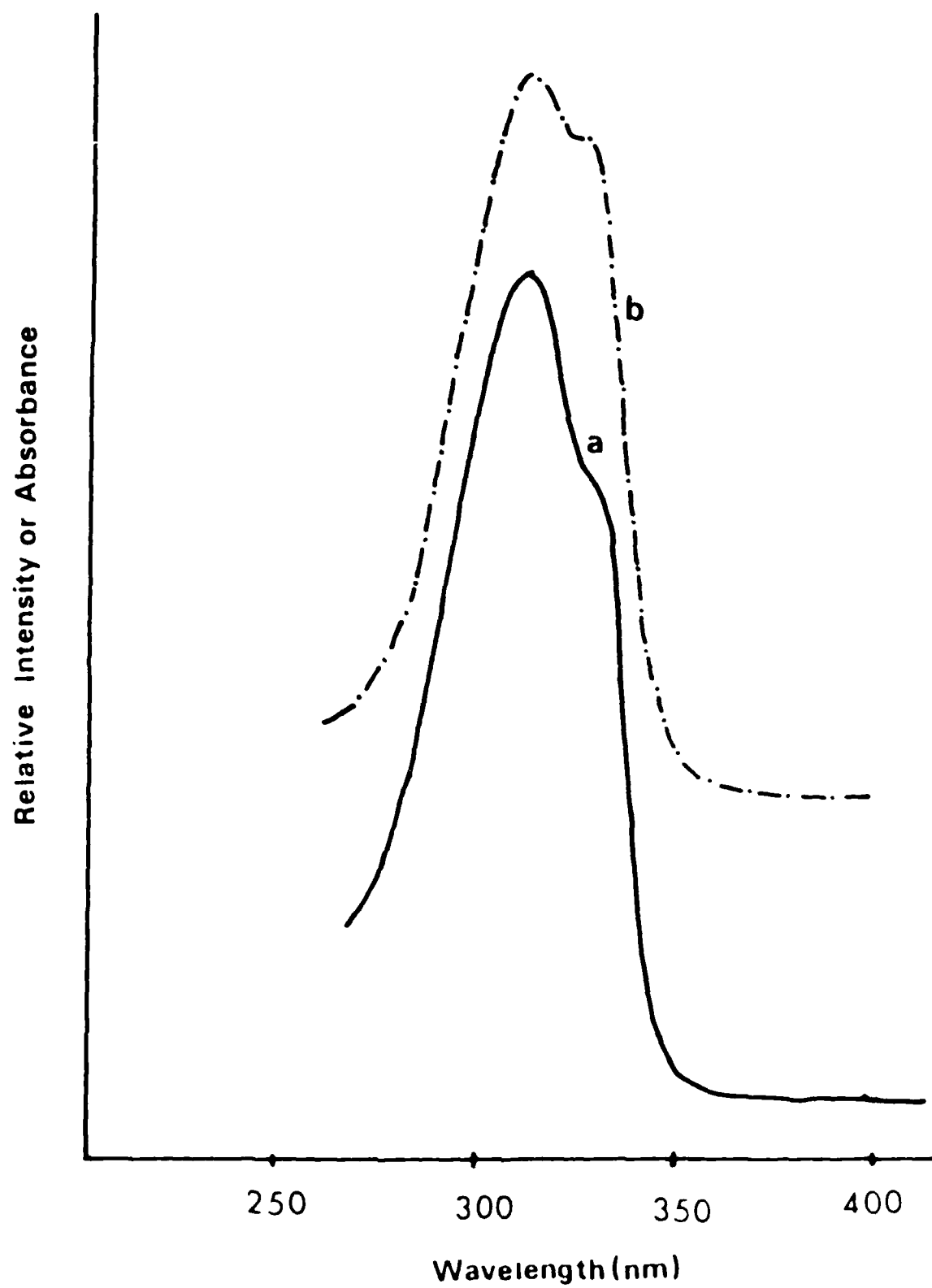
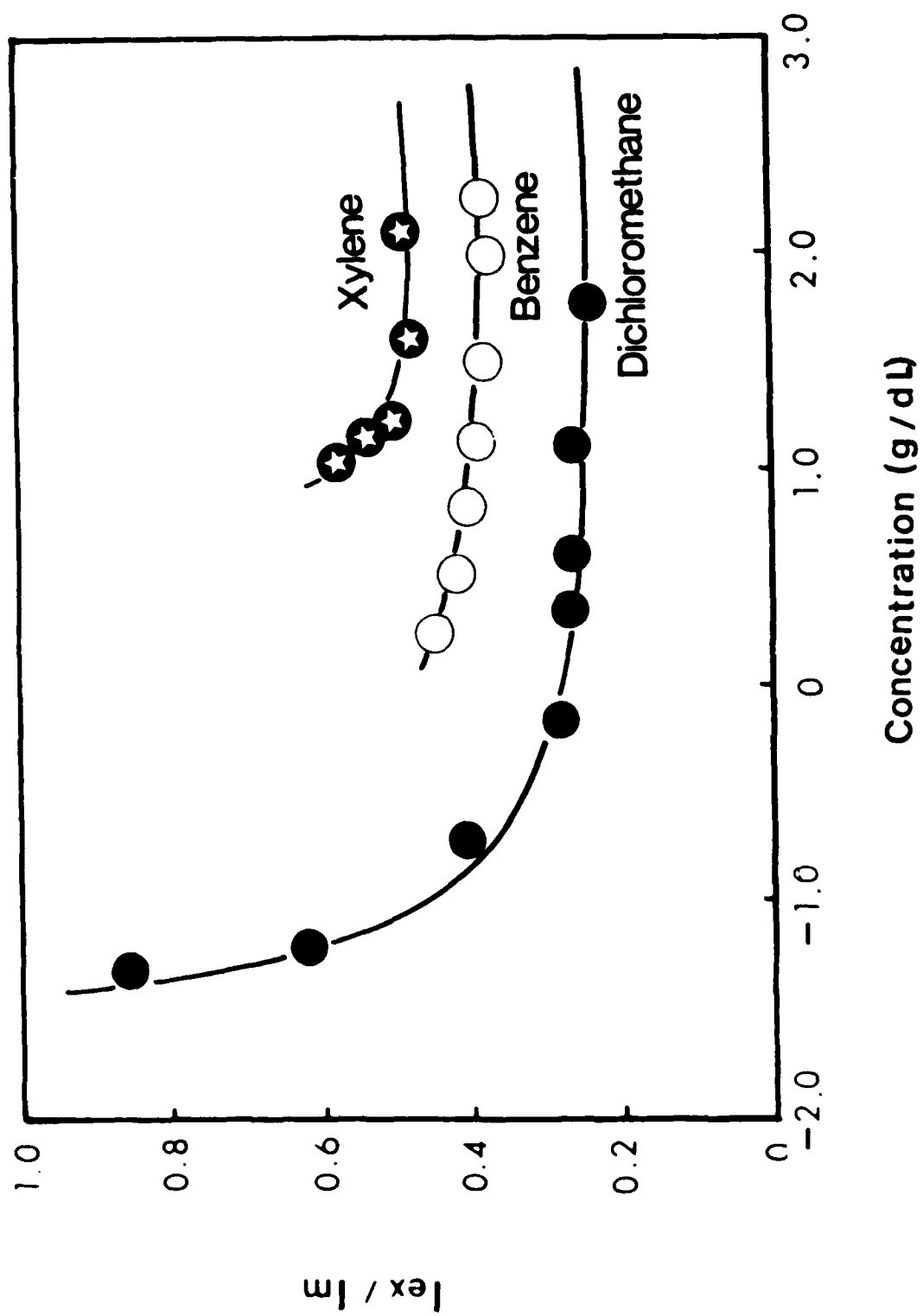
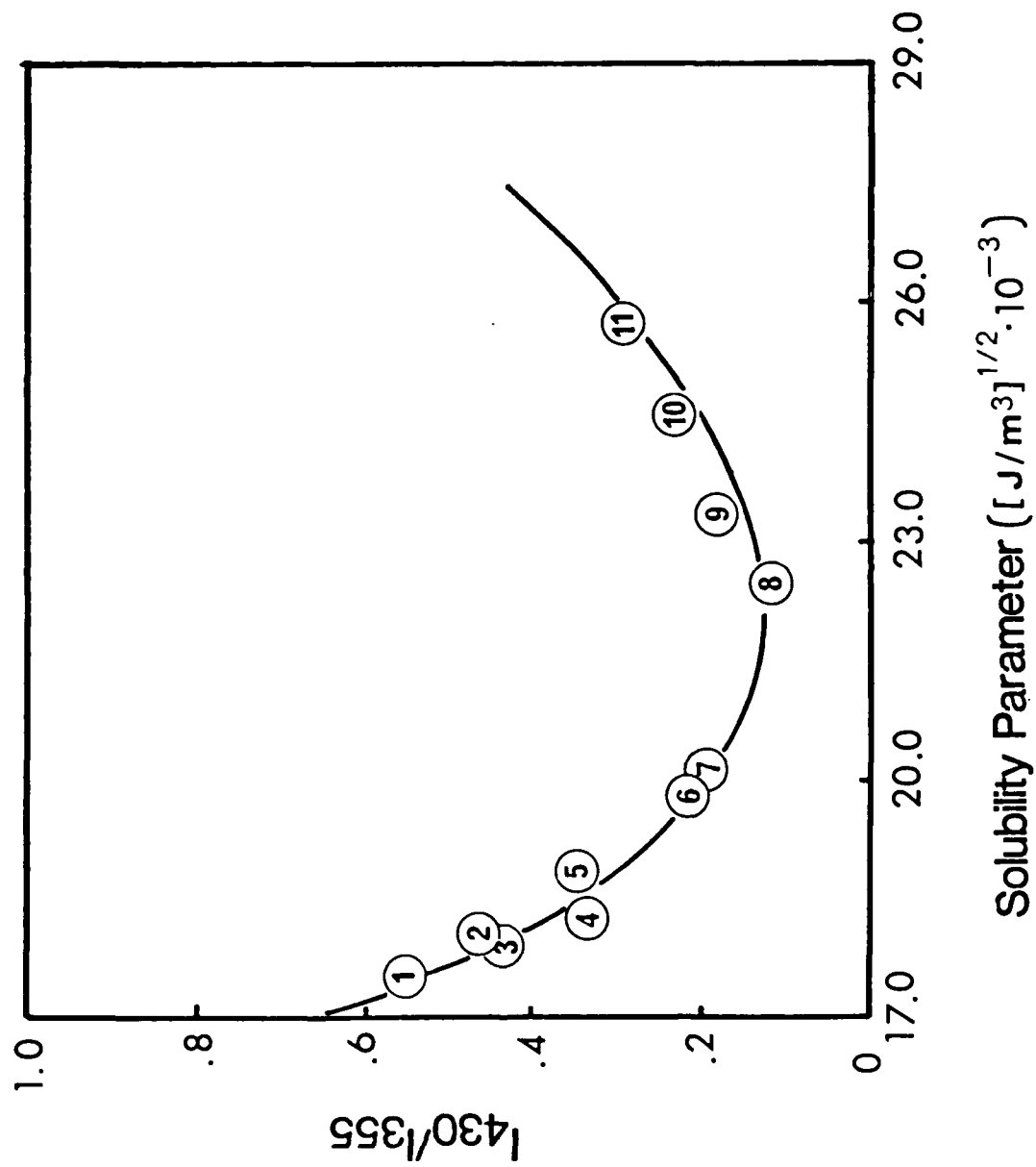


Fig 10







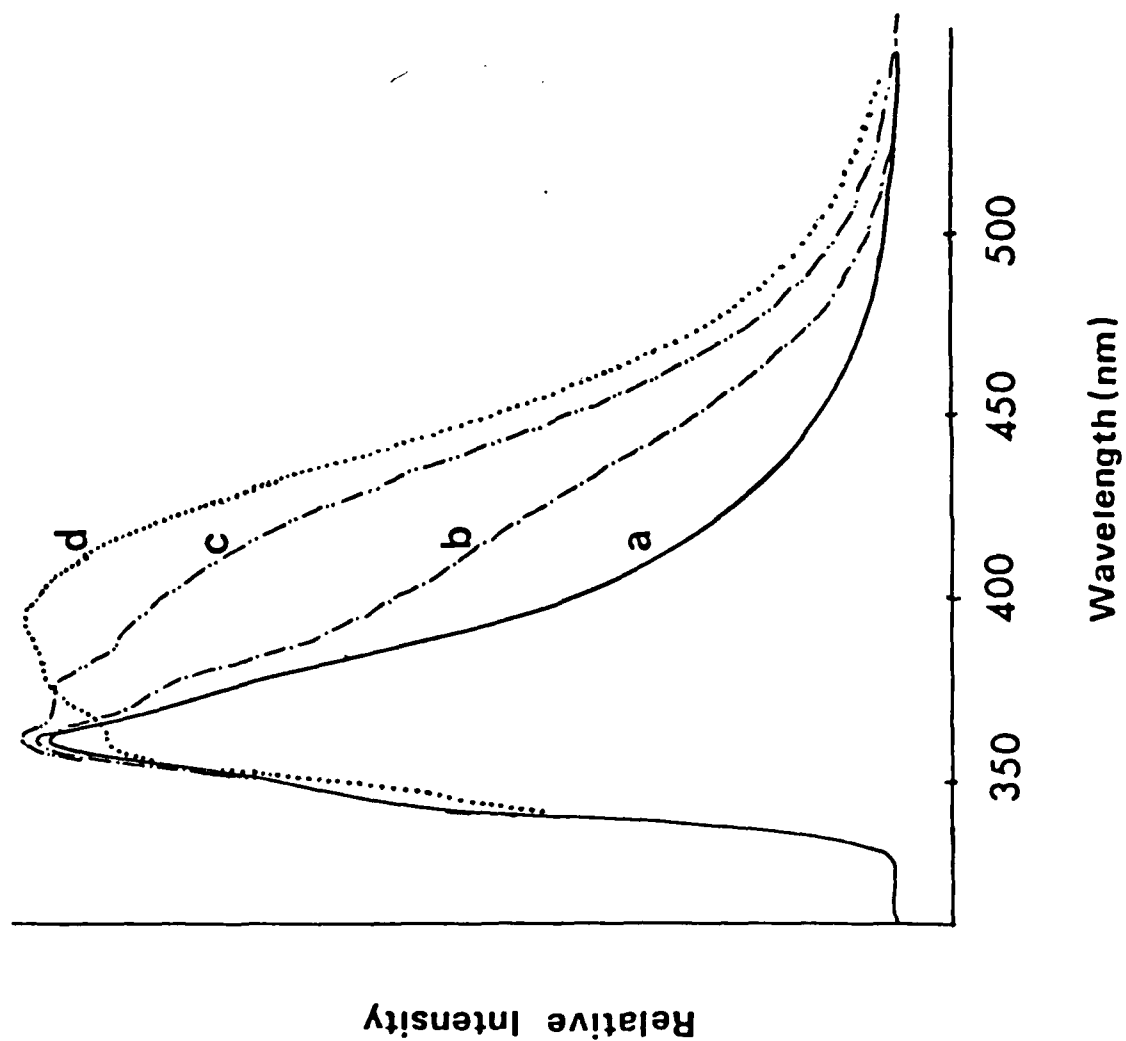


Fig. 13

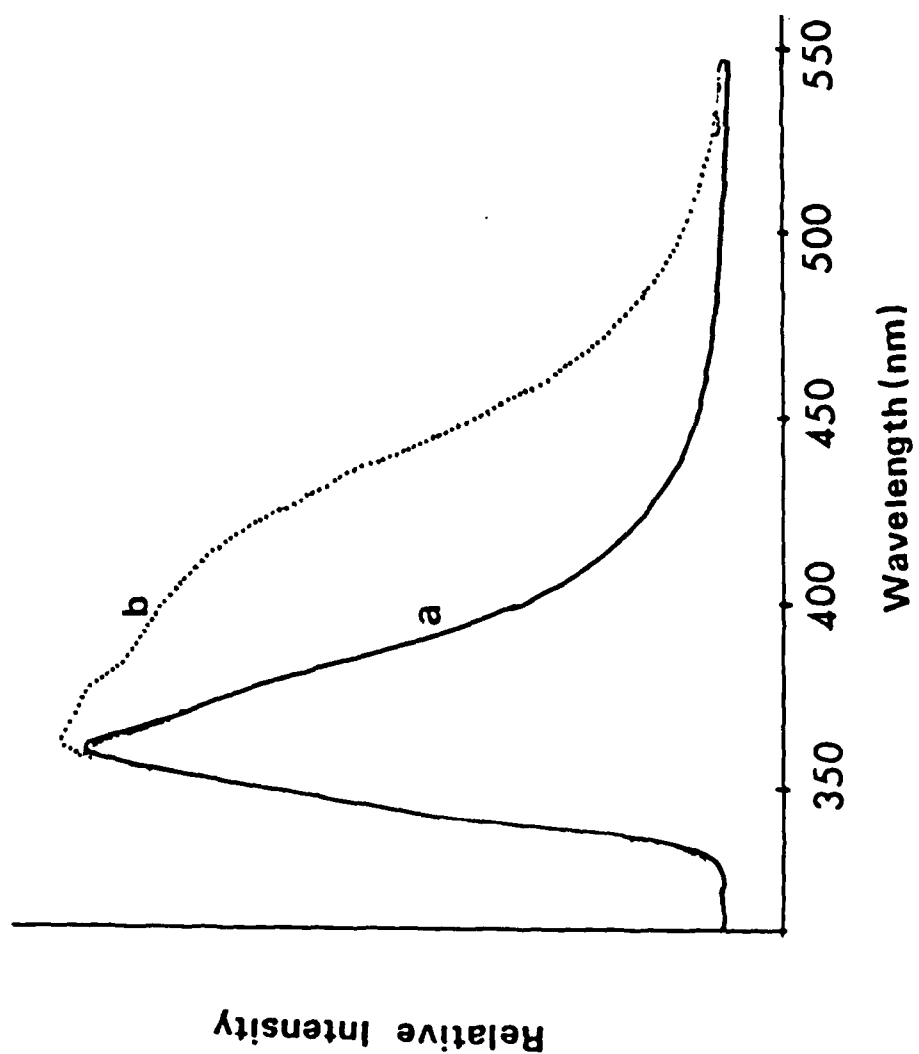
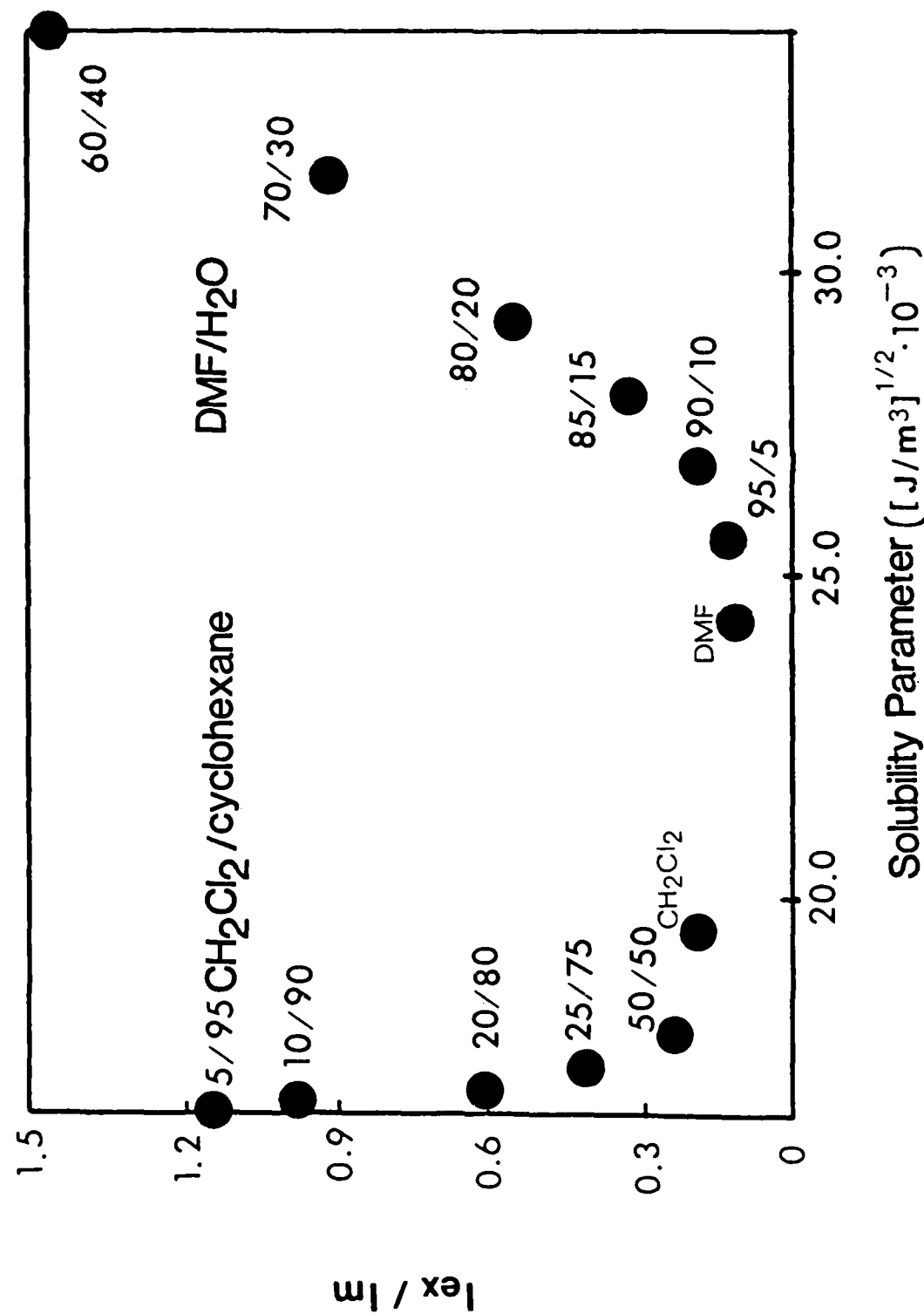


Fig. 14



Fig. 15



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